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Ablation behavior of boron nitride based ceramic composites reinforced by continuous silicon oxynitride fiber

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Abstract

Continuous silicon oxynitride fiber reinforced boron nitride matrix (Si–N–O_f/BN) composite has been recognized as a promising microwave transparent radome material. In the present study, the ablation behavior and properties of the Si–N–O_f/BN composites under an oxyacetylene torch ablation environment were investigated. The average linear and mass ablation rates of the composites decreased with the increasing of the fabrication temperature and were 0.132 mm s^{-1} and 0.057 g s^{-1} for the 1200 °C fabricated composites. The ablation products mainly consisted of glassy SiO_2 and B_2O_3, and highly crystallized BN. The ablation center involved three different actions: decomposition of the Si–N–O fibers and sublimation of the BN matrix, oxidations of the matrix and the reinforcing fibers, and thermal treatment of the BN matrix beneath the covering SiO_2 film.

Keywords: B. Composites; C. Thermal properties; D. Nitrides; Ablation

1. Introduction

A radome is a structural, weatherproof enclosure in hypersonic aircrafts or re-entry vehicles that protects radar antenna from outside environmental erosion and high aerodynamic load [1,2]. During the high velocity re-entry stage, the harsh environment would induce extreme high aerodynamic pressure and thermal flux on the radome surface [3]. Thus, to avoid rough ablation surface or even shape deformation, the radar protective component must be strong enough to sustain the thermal shock while maintaining its structural integrity [4].

Ceramic fiber reinforced boron nitride (BN) composites (FCMs) have been recognized as prospective wave transparent materials for they combine the high refractory, good dielectric properties and excellent thermal shock resistance of BN ceramic with a ductile fracture behavior [5–9]. However, the reinforcing fibers available for the BN based composites are quite limited. Quartz fiber is a commonly used reinforcement in radome materials. However, due to the crystallization-prone nature of quartz fiber at high temperatures, the fabrication temperature of the composites is relative low, typically 800 °C [6,10]. Consequently, it produces a low bonding strength between the fiber and the matrix, leading to a low mechanical strength of the composites. Moreover, moisture and oxygen vulnerable BN matrix would be generated with a low fabrication temperature, especially for those BN matrix obtained from chemical vapor infiltration (CVI) and precursor pyrolysis methods [11,12]. BN fiber displays excellent high temperature performance and has been applied to prepare BN_f/BN composites [7,8]. In spite of this, BN fiber exhibits a relative low oxidation temperature of 900 °C, which restricts it from long time use at high temperatures. Pure BN_f/BN composites also suffer from massive transmissivity loss above 2000 °C causing by the high conductivity in the surface layer [13,14]. In comparison, precursor pyrolysis derived silicon nitride-based ceramic fibers have received renewed attention because of their designable composition and favorable high temperature properties. Silicon oxynitride fiber, for instance, is reported to be

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structurally and mechanically stable up to 1200 °C in air and 1400 °C in Ar gas, respectively [15,16]. Our previous investigations have shown that the Si–N–O_f/BN composites display an inspiring bending strength of 131.0 MPa at 1300 °C, as well as a low dielectric constant of 3.7 at 1600 °C, reflecting the highly potential of the composites [17,18].

The current study is dedicated to evaluate the ablation performance of the Si–N–O_f/BN composites for their potential applications in extreme severe environment. The concerns include the specific linear and mass ablation rates the different temperature fabricated composites, the ablated microstructure, and the different ablation behaviors at the ablation center.

2. Experimental procedures

Liquid borazine ($B_3N_3H_6$) and continuous Si–N–O fibers were used as raw materials. Liquid borazine, with a low density of 0.86 g cm^{-3}, was synthesized and purified according to our previous work [19]. The Si–N–O fibers ($Si_{1.00}N_{1.17}O_{0.47}$ in chemical composition) were produced by the National University of Defense Technology. The fibers display a density of 2.23 g cm^{-3}, an average diameter of 12 μm and an average tensile strength of 1.4 GPa. Prior to composites fabrication, the Si–N–O fibers were clamped in a mold unidirectionally with a fiber volume fraction of ~45%.

The preparation of the Si–N–O_f/BN composites basically involved three individual steps [17]: (i) liquid borazine was infiltrated into the Si–N–O fabrics via a vacuum-assisted approach; (ii) self-cross-linking and solidification of the precursor was proposed by a stepwise thermal heating up to 70 °C and hold for 48 h, followed by another holding at 90 °C for another 24 h; and (iii) the polymer-matrix composites were pyrolyzed into ceramic matrix composites at 800–1200 °C for 1 h under N_2 gas. Four repeated borazine infiltration and pyrolysis cycles were applied to obtain the final composites.

The bulk density of the specimens was obtained by measuring their dry weight and external dimensions. The theoretical density was calculated using the mixture rule, in which the densities used for the 800 °C, 1000 °C and 1200 °C derived BN matrix were 1.76 g cm^{-3}, 1.86 g cm^{-3} and 1.93 g cm^{-3} respectively. The relative density was defined as the quotient of the bulk density to the theoretical density.

The phase composition of the composites was identified by X-ray diffraction (XRD, D 8 Advance, Bruker/Axs Corp., Germany) using Ni-filtered CuK_α radiation. The morphology of the obtained composites and the ablated composites were observed by scanning electron microscopy (SEM, Hitachi S-4800). The surface state of the ablated composites was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250, Al K_α radiation, U.S.A).

The ablation tests were carried out under an oxyacetylene flame in air following GJB323A-96. The pressures of oxygen and acetylene were 0.25 MPa and 0.04 MPa, respectively. The surface temperature of the specimen was ~3000 K with a heat flux of 4200 kW m^{-2} (10% error). The distance between the tip of the gun and the specimen surface was 10 mm and the exposure time under the torch flame was 10 s. Three samples with dimensions of 30 mm × 30 mm × 5 mm were examined in each division. Prior to the ablation test, the samples were ground so as to obtain high parallel surfaces between the up and the bottom. The linear and mass ablation rates (R_l and R_m) are defined as follows:

$$R_l = (h_0 - h_1)/t$$

$$R_m = (m_0 - m_1)/t$$

where h_0 and h_1 are the thickness of specimen before and after ablation; m_0 and m_1 represent the weight before and after ablation; and t is the ablation time.

3. Results and discussions

3.1. Phase characterization and ablation properties

A key aspect of the preparation of the Si–N–O_f/BN composites is the use of the low-viscosity borazine precursor which permits easy wetting and infiltrating of the fiber lay-ups [20,21]. The high inorganic converting ratio of the precursor (> 80% in this study) also leads to an inspiring processing efficiency [22]. Fig. 1 shows the morphologies of the Si–N–O_f/BN composites. As can be seen, continuous BN matrix network was already built up after two infiltration and pyrolysis cycles; and with four cycles, a desirable dense composite was obtained. The final density of the composites was 1.84–1.90 g mm^{-3}, corresponding to the relative density of 92.0%–93.3%, as listed in Table 1. Nevertheless, Fig. 1d reveals the existence of microcracks within the BN matrix, probably caused by matrix shrinkage during pyrolysis. These microcracks would facilitate oxygen penetration when exposed to high oxygen potentials [23,24].

Fig. 2 shows the XRD profiles of the Si–N–O fibers, the different temperature derived BN matrix and the 1200 °C fabricated composite. As shown, the silicon oxynitride fiber is amorphous in microstructure with two broad diffraction peaks located at around 25° and 68° [15]. For the BN matrix, the broad diffraction peaks around 25°, 43° and 78° are attributed to the diffractions of (002), (10) and (11) planes of turbostratic BN [25]. Hence, the profile of the Si–N–O_f/BN composites could be decomposed into two individual profiles belonging to the reinforcing fiber and the BN matrix, as illustrated in Fig. 2d. While maintaining turbostratic in microstructure, the density and crystalline degree of the derived BN matrix was found to increase with the pyrolysis temperature. As the pyrolysis temperature was elevated from 800 °C to 1200 °C, the density the BN matrix increased from 1.76 g cm^{-3} to 1.93 g cm^{-3}, alongside the decreasing of interlayer spacing [d (002)] from 3.58 Å to 3.41 Å. The decreasing trend of the interlayer spacing was also reflected by the shifting of (002) diffraction peak towards higher angles as the pyrolysis temperature increased (Fig. 2b–d). With an interlayer spacing close to commercial h-BN (3.33 Å), the 1200 °C derived BN matrix was expect to behave a good oxygen resistance [26].

The ablation properties of the Si–N–O_f/BN composites are listed in Table 1. Both the average linear ablation rate and mass ablation rate of the composites decreased with the